

FORMATION OF POLYCYCLIC AROMATIC HYDROCARBONS AND ELIMINATION OF ALIPHATIC SUBSTITUENTS IN SECONDARY REACTION OF FLASH PYROLYSIS TAR

Jun-ichiro Hayashi, Tsutomu Kawakami, Tomohiro Taniguchi,
Katsuki Kusakabe and Shigeharu Morooka
Department of Chemical Science and Technology,
Kyushu University, Fukuoka 812, Japan

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) derived from coal tar and pitch are very useful for starting materials of various specialty chemicals. To produce PAHs, flash pyrolysis of coal is attractive because its tar yield is much higher than that of other carbonization processes with slow heating rates.¹ However, the quality of flash pyrolysis tar is rather inferior to that of slow pyrolysis tar.²

Coal pyrolysis consists of two reactions in series: the primary reaction of the macromolecular network of coal to tar; and the secondary reaction of tar in the gas phase.³

Division of reaction zones is indispensable for the quantitative examination of time- and temperature-dependent changes in molecular composition of tar, as indicated by Xu et al.⁴ and Serio et al.⁵ who separated these reaction zones by using the two-stage reactors comprising of a fixed bed of coal and a tubular reactor connected downstream.

In the present study, the two-stage concept is applied to the flash pyrolysis of a subbituminous coal with a fluidized-bed reactor divided into two zones: a dense bed for the primary reaction and a freeboard above the dense bed for the secondary reaction. Tar is processed in the freeboard at a temperature different from that in the dense bed. PAHs in the tar is characterized by FIMS and ¹H-NMR after the separation based on ring structure of molecule. The temperature dependence of the following features are determined: molar yield of homologues having the same ring structure; and number-based distribution of aliphatic carbons per molecule for each homologue.

EXPERIMENTAL

Flash pyrolysis

Wandoan subbituminous coal (C:76.2, H:5.77, N:1.03 in wt.%, daf) was employed for the experiment. The coal sample was pulverized, sized to 0.37-0.74 mm and dried in vacuo at 100°C. The fluidized-bed reactor was divided into dense and freeboard zones, and they were heated separately with external furnaces whose temperatures were independently controlled. The temperature was set in the range of 600-900°C for the freeboard and fixed at 600°C for the dense bed. Coal particles were introduced into the dense bed at a constant rate of 4.2 mg/s. The total gas flow rate was 33.3 ml/s at 20°C. The total residence time of tar vapor was 4.0-4.5 s.

Separation and characterization of tar samples

The tar was separated into benzene-soluble (asphaltene) and insoluble (preasphaltene) portions. The asphaltene was further fractionated into saturates, aromatic hydrocarbons, nitrogen-containing compounds, hydroxylic compounds and the uneluted components by the elution chromatography with neutral alumina.⁶ The yield of the uneluted component was added to that of the preasphaltene.

The aromatic hydrocarbons was further separated by HPLC on the basis of ring structure with a semipreparative NH_2 column (Hiber Column, Merck) with *n*-heptane as the mobile phase.⁷ By this method, aromatics were classified by number of double bonds per molecule (d.b.) into 3 (monocyclic), 5 (dicyclic), 6 (dicyclic), 7 (tri-cyclic), 8 (tetracyclic), 9 (tetracyclic), 10 (pentacyclic), 11 and 12 (pentacyclic and greater PAHs). Each double-bond fractions were analyzed by $^1\text{H-NMR}$ and FIMS.

RESULTS AND DISCUSSION

Temperature dependence of yield and chemical composition of tar

Figure 1(a) shows the effect of freeboard temperature on the tar yield. When fine coal particles were fed into the dense bed, most particles were entrained by the gas flow. When coal particles were in the size range of 0.21-0.42 mm, however, entrainment hardly occurred. The tar yield by the pyrolysis of the 0.21-0.42 mm particles was virtually identical to that shown in Figure 1. Thus the tar evolution was completed in a short period compared with the residence time of gas in the freeboard.

Figure 1(b) shows yields of components normalized by total tar yield as a function of freeboard temperature. There are three patterns of temperature dependence. The yield of PAHs and nitrogen-containing compounds increases with increasing temperature and then attains ca. 80 wt.% of the total tar yield at 900°C, while that of saturates and preasphaltene decreases monotonously above 600°C. Ethers and hydroxylic compounds show their maximum yield at 700°C. It is clear that the increase in yield of PAHs is compensated by the decrease of the other components, and their roles as precursors of PAHs vary by component.

Yield and structural distribution of PAH component

The FIMS analysis reveals that a PAH molecule has 5 to 12 double bonds. Figure 2 shows the FIMS spectra of the 6, 7 and 8 d.b. fractions separated from tar at 800°C. The spectra shown in Figure 2(a) consist of two series of signals appearing at the mass number $152+14n$ and $154+14n$ (n = integer). The former is attributed to the homologue of acenaphthylene (MW = 152) and fluorene (MW = 166), and the latter to that of biphenyl (MW = 154). These homologues have the same double-bond number of 6. Figure 2(b) and (c) show that the 7 and 8 d.b. fractions are composed of the homologues of phenanthrene (or anthracene) and pyrene (or fluoranthene) respectively. Each fraction is a mixture of compounds having the same number of aromatic rings and a different number of methylene units. Peaks with the smallest mass in the FIMS spectrum of each homologue are assigned to the PAHs listed in Table 1.

All the PAH homologues are composed of an unsubstituted PAH and its alkyl-derivatives. Since alkyl substituents are sensitive to the reaction temperature, the total mass of compounds is not a reliable indicator of the yield of homologue. Therefore, the mass of a substituted PAH having aliphatic carbons is converted to that of an

unsubstituted PAH. Figure 3 shows the yield of the 6-12 d.b. homologues. All of them monotonously increase with increasing temperature. This suggests that the formation of PAHs below 900°C is predominant over the soot formation that causes a decrease in the PAH yield. The homologues of 6, 7 and 8 d.b. are most abundant. Each of them comprises more than 1.0 wt% of coal on daf basis at 900°C. The temperature profile of PAH yield varies by homologue. The larger the d.b. number, the higher the temperature at which the slope changes steeply. The yields of the 11 and 12 d.b. homologues increase remarkably above 700°C in accord with the evolution of hydrogen gas. In this temperature range, a part of the 11 and 12 d.b. homologues is formed via condensation of smaller aromatic rings, and hydrogen gas is produced as a result.

Aliphatic carbons attached to aromatic ring

The number-based distribution of aliphatic carbons (methylene units) per molecule is shown in Figure 4 for the 8 and 9 d.b. homologues. The FIMS analysis combined with the HPLC separation allows the determination of the yield of molecules composed of a specific aromatic ring and a specific number of aliphatic carbons. The number of aliphatic carbons per molecule is distributed over the range of 0 to 9 at 600°C, where aliphatic carbons are most abundant. Teo and Watkinson⁸ pyrolyzed coals in a spouted bed and characterized the molecular composition of tar by HPLC and GC-MS. They found that the number of aliphatic carbons was less than four for aromatic homologues with 1 to 4 rings. Our results, on the other hand, reveal that PAHs bearing more than four or five aliphatic carbons are abundant, particularly in low-temperature tars.

The distribution shown in Figure 4 moves toward the small-number side with increasing secondary reaction temperature. The mole fraction of unsubstituted PAHs is only ca. 5% in the homologues obtained at 600°C, but is ca. 50% at 900°C. The temperature dependence of the yield of substituted molecules varies with the number of aliphatic carbons. In the case of the 7 d.b. homologue, the yield of C₁ and C₂ derivatives shows a maximum at 800°C, while that of C₃ and C₄ derivatives at 700°C. The yield of molecules having more than five aliphatic carbons decreases monotonously over the temperature range tested.

Classification of aliphatic carbons

The NMR data of each d.b. fraction are analyzed by assuming the existence of only methyl-, ethyl- and propyl-chains. This is reasonable because the β -hydrogen content is at most half that of α -hydrogen even at 600°C, where the ratio of β - to α -hydrogen is the highest for all the fractions. The number of chains is given by the following equations.

$$N(\text{propyl}) = N(H_\gamma)/3 \quad (1)$$

$$N(\text{ethyl}) = [N(H_\beta) - 2N(\text{propyl})]/3 \quad (2)$$

$$N(\text{methyl}) = [N(H_\alpha) - 2N(\text{ethyl}) - 2N(\text{propyl})]/3 \quad (3)$$

$$N(\alpha, \alpha\text{-methylene}) = N(H_{\alpha, \alpha})/2 \quad (4)$$

where $N(H_\alpha)$, $N(H_\beta)$ and $N(H_\gamma)$ are respectively the number-based content of α -, β - and γ -hydrogen normalized by the total hydrogen content. The total number of aliphatic carbons is

$$C_{al} = N(\text{methyl}) + 2N(\text{ethyl}) + 3N(\text{propyl}) + N(\alpha, \alpha\text{-methylene}) \quad (5)$$

The sum of the number of protonated and alkylated aromatic carbons is

$$C_{pa} = N(\text{methyl}) + N(\text{ethyl}) + N(\text{propyl}) + N(H_{ar}) + 2N(\alpha, \alpha\text{-methylene}) \quad (6)$$

where $N(H_{ar})$ is the number-based content of aromatic hydrogens. The total number of aromatic carbons is given as

$$C_{ar} = C_{pa} + C_b \quad (7)$$

where C_b is the number of bridgehead carbons. The ratio of C_{pa} to C_b is determined from the ring structure. The value of C_{pa}/C_{ar} is calculated from the composition of PAHs by the FIMS analysis in all the fractions of different d.b., and is for instance 10/14 for the 7 d.b. homologue. The averaged number of aliphatic carbons per molecule is

$$N(CH_2) = C_{al}/(C_{ar}/ARC) \quad (8)$$

where ARC is the averaged number of aromatic carbons per molecule. The value of $N(CH_2)$ can also be determined by the FIMS data as shown in Figure 4. The values of $N(CH_2)$ calculated from Equation (8) are in agreement with those by the FIMS analysis within an error of 10%.

Figure 5 exhibits the composition of aliphatic carbons in the fractions of 8 and 9 d.b. The number of α -, β - and γ -carbons decreases with increasing temperature. The number of α, α -carbons is independent of temperature in the range of 600-800°C, while it decreases above 800°C.

Figure 6 shows the number of methyl and ethyl chains per molecule for the 8 and 9 d.b. fractions. The number of ethyl chains decreases by 65-85% in the range of 600-700°C, while that of methyl chains hardly changes. This result suggests that the decrease in the number of α -carbons at 600-700°C is due to detachment of ethyl and propyl chains by the selective bond cleavage at aryl- α positions.

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Table 1. Molecular mass of initial peaks in FIMS spectra of each d.b. homologue.

d.b.	Molecular mass
5	128 (naphthalene)
6	152 (acenaphthylene), 154 (biphenyl)
7	178 (anthracene, phenanthrene)
8	202 (pyrene and fluorentene)
9	226, 228 (chrysene)
10	252 (benzo(a)pyrene, perylene), 254 (phenylphenanthrene)
11	276, 278 (picene, dibenzanthracene)
12	300 (coronene), 302 (dibenzpyrene), 304 (phenanthrenoanthracene)

^a Compounds indicated in parenthesis are PAHs to which the peaks are assigned.

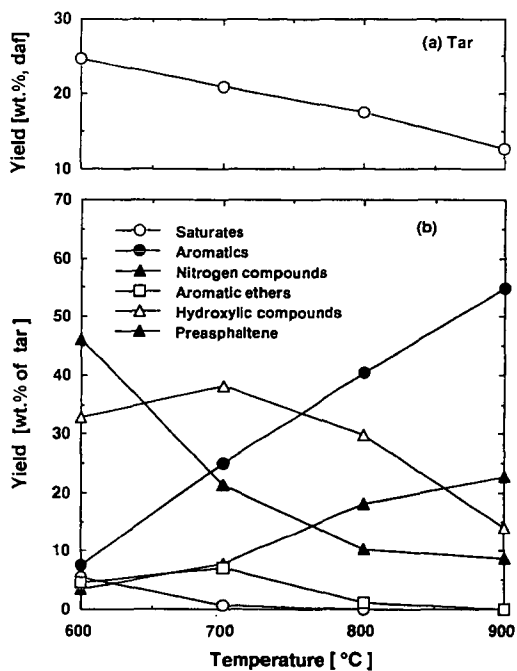


Figure 1. Temperature dependence of yield and composition of tar.

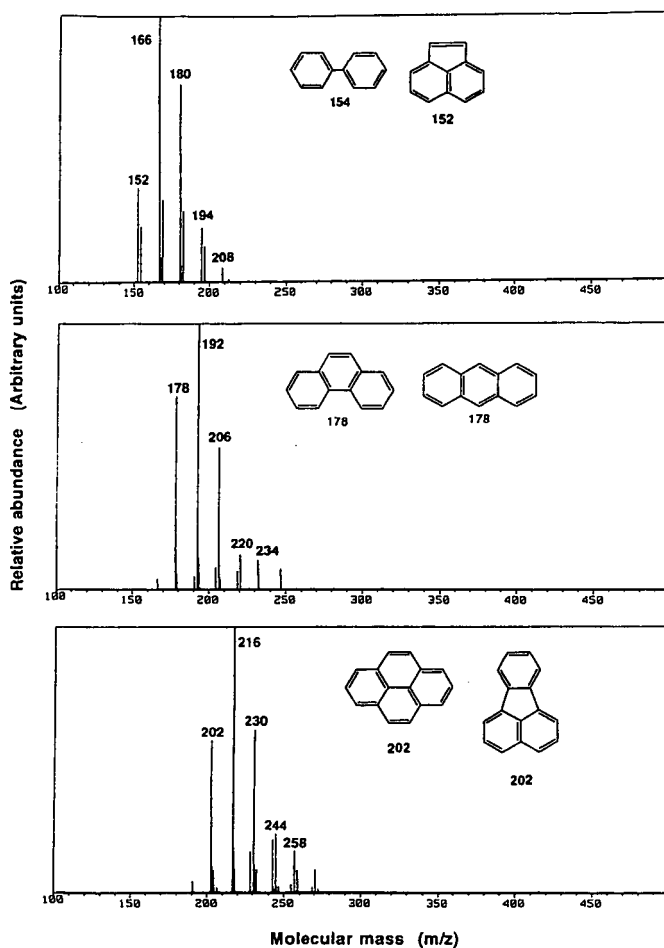


Figure 2. FIMS spectra of 6, 7 and 8 d.b. fractions at 800°C.

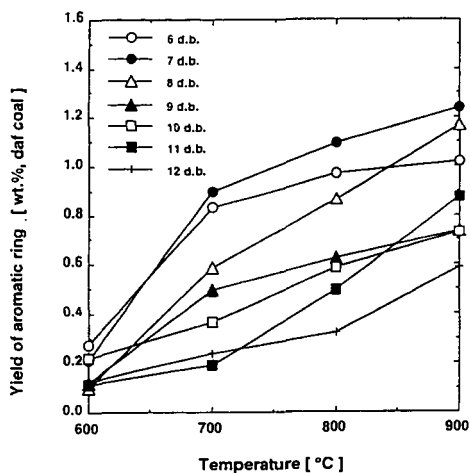


Figure 3. Yield of individual double-bond homologues converted into that of unsubstituted PAH.

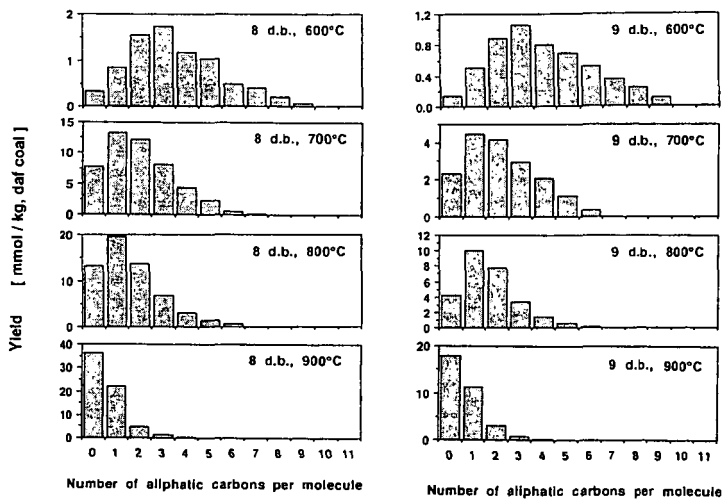


Figure 4. Distribution in number of aliphatic carbons per molecule for 8 and 9 d.b. homologues.

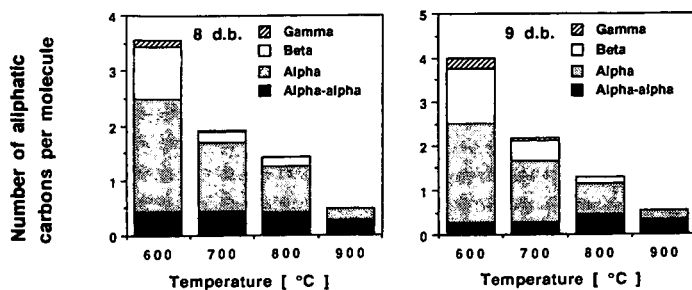


Figure 5. Composition of aliphatic carbons in 8 and 9 d.b. fractions.

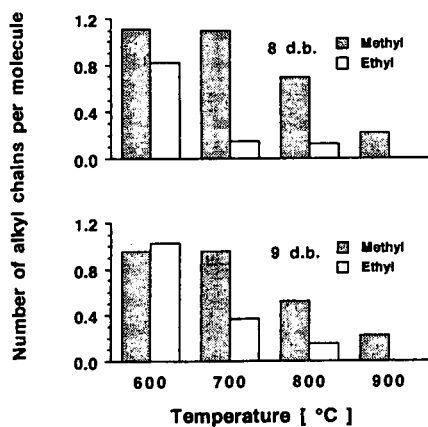


Figure 6. Number of methyl and ethyl chains per molecule for 8 and 9 d.b. fractions.